USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 354
VOLATILE ORGANIC COMPOUND ANALYSIS IN WATER

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1 SCOPE AND APPLICABILITY

This Standard Operating Procedure (SOP) describes the analysis of volatile organic compounds (VOCs) in water by gas chromatography/mass spectrometry (GC/MS). This SOP is based on EPA Method 524.2, Revision 4.1, 1995. Deviations from the reference methods are described in Appendix A. Analytes and quantitation limits (QLs) are listed in Appendix B.

This SOP is applicable to the analysis of surface water, ground water, and drinking water for VOCs, including SDWA compliance samples. It is not appropriate for NPDES compliance samples. The quality control (QC) criteria specified in this SOP meet compliance criteria for drinking water monitoring projects.

2 METHOD SUMMARY

VOCs are purged from a 25-mL sample in a fritted sparge cell, separated in a narrow bore fused silica GC column, and detected by a mass spectrometer. Target volatile organic compounds are identified in the sample by comparing the mass spectra to the mass spectra in the National Institute of Standards and Technology (NIST) library and the GC retention times of the target analytes to retention times of standards analyzed under the same conditions as samples. Each compound is quantitated using average response factors from the most recent initial calibration.

3 DEFINITIONS

A list of terms and definitions specific to this procedure appears below. For terms and acronyms in general use at the EPA Region 9 Laboratory refer to Appendix A of the Laboratory Quality Assurance Plan.

Calibration Standard (CAL) –The CAL solutions are used to calibrate instrument response with respect to analyte concentration. CAL solutions are prepared in the laboratory by diluting vendor supplied materials (pure material or solutions of analytes at certified concentrations).

Mass to charge ratio (m/z) – equals ion mass (in u) divided by number of unit charge for the ion.

4 SAFETY & HEALTH

All laboratory personnel must follow health and safety requirements outlined in current versions of the EPA Region 9 Laboratory Chemical Hygiene Plan (CHP) and the Region 9

Laboratory Business Plan. Potential hazards specific to this SOP as well as pollution prevention and waste management requirements are described in the following sections.

4.1 Chemical Hazards

Due to the unknown and potentially hazardous characteristics of samples, all sample handling and preparation should be performed in a well-vented laboratory fume hood.

The toxicity and carcinogenicity of each reagent used in this method may not be fully established. Each chemical should be regarded as a potential health hazard and exposure to them should be minimized by good laboratory practices. Refer to the CHP for further information and the Material Safety Data Sheets located in Room 118 (library) and the LAN at I:\MSDS IMAGES for additional chemical-specific information.

4.1.1 Methanol

Methanol is the primary solvent used for the preparation of standards in these procedures. Methanol is harmful if inhaled and may be fatal or cause blindness if ingested. Symptoms of overexposure via inhalation are drowsiness and intoxication, headache, visual disturbances leading to blindness, coughing, and shortness of breath, collapse, and death at high concentrations. Skin contact may result in absorption producing toxic effects. Repeated skin contact may cause burning, itching, redness, blisters or dermatitis. Eye contact can cause burning, watering, redness and swelling. High vapor concentration will result in similar symptoms in the eyes. Medical attention must be sought whenever symptoms of inhalation or ingestion are observed as many effects are delayed due to the slow rate of metabolism.

Methanol is classified as a flammable solvent and must be handled accordingly. Use methanol in a laboratory fume hood with appropriate personal protective equipment (laboratory coat, nitrile gloves and safety glasses). Store methanol in a flammable storage cabinet away from oxidizers and sources of ignition.

4.1.2 Hydrochloric acid

Hydrochloric acid is a corrosive poison. Liquid and mist cause severe burns to all body tissues and may be fatal if swallowed or inhaled. Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms of exposure by inhalation may include irritation of the nose and throat, and labored breathing. Do not get acid in eyes, on skin, or on clothing. Skin contact can cause redness, pain, and severe skin burns. In case of contact, immediately flush eyes or skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes.

When diluting an acid, the acid should always be added slowly to water and in small amounts. Never use hot water and never add water to the acid. Water added to acid can cause uncontrolled boiling and splashing. Concentrated hydrochloric acid is incompatible with many substances and highly reactive with strong bases, metals, metal oxides, hydroxides, amines, carbonates and other alkaline materials. Acids are incompatible with materials such as cyanides, sulfides, sulfites, and formaldehyde.

4.2 Equipment and Instruments

Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

4.3 Pollution Prevention

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA Region 9 Laboratory places pollution prevention as the management option of first choice with regard to environmental management. Whenever feasible, laboratory personnel shall use pollution prevention techniques to address waste generation. When wastes cannot be feasibly reduced, recycling is the next best option. The *EPA Region 9 Laboratory Environmental Management System* provides details regarding efforts to minimize waste.

Minimize waste through the judicious selection of volumes for reagents and standards to prevent the generation of waste due to expiration of excess materials. Reduce the volume of any reagent or standard described in Sections 7.2 or 7.3 so long as good laboratory practices are adhered to regarding the accuracy and precision of the glassware, syringes, and/or analytical balances used to prepare the solution. Reducing the concentration of a reagent is not allowed under this procedure because the impact of such a change on the chemistry of the procedure must be assessed prior to implementation.

Reduce the toxicity of waste by purchasing lower concentration standards, lower concentration reagents, and solutions to replace neat chemicals whenever possible. However, do not change the concentrations of standards and reagents specifically designated in this SOP.

4.4 Waste Management

The EPA Region 9 Laboratory complies with all applicable rules and regulations in the management of laboratory waste. The laboratory minimizes and controls all releases

from hoods and bench operations. All analysts must collect and manage laboratory waste in a manner consistent with EPA Region 9 Laboratory SOP 706 *Laboratory Waste Management Procedure*. Solid and hazardous wastes are disposed of in compliance with hazardous waste identification rules and land disposal restrictions. If additional guidance is needed for new waste streams or changes to existing waste streams, consult with EPA Laboratory Safety, Health, and Environmental Manager (LaSHEM) or ESAT Health and Safety and Environmental Compliance Task Manager or designees.

This procedure generates the following waste streams:

Waste Stream Description	Waste Label	Hazard Properties
Laboratory solid waste (gloves, contaminated paper towels, disposable glassware, etc.)	Non-hazardous Waste	Not applicable
Aqueous acidic VOC waste (wastewater, hydrochloric acid, trace halogenated volatile compounds)	Hazardous Waste	Corrosive
Methanol waste (methanol, halogenated volatile compounds)	Hazardous Waste	Flammable, toxic
Waste pump oil (trace halogenated volatile compounds)	Hazardous Waste	Toxic

5 SAMPLE HANDLING AND PRESERVATION

5.1 Containers and Required Sample Volume

Samples should be collected in pre-cleaned 40-mL screw cap vials equipped with Teflon-faced silicone septum. Volume collected should be sufficient to allow for replicate analysis yet minimize waste disposal. Three 40-mL vials should be sufficient to meet these objectives.

5.2 Internal Chain-of-Custody

Verify sample IDs and dates and times of collection against the chain-of-custody form. If discrepancies are noted, inform the sample custodian.

Update the LIMS internal custody form when sample containers are moved from the designated sample location. Change the container disposition to "active out" and the location to the appropriate room number. At the end of the day, return sample containers to the "Home" locations. Update the LIMS using the "return to home

location" feature and update container disposition to "available in". Verify that your initials are recorded whenever you update the LIMS custody information.

Samples for VOC analysis are delivered by the Sample Custodian to Room 201, logged into the Laboratory Information Management System (LIMS), and transferred to the sample refrigerator (or freezer, as applicable).

5.3 Preservation Verification

Unless specified otherwise in project plans or the COC, samples should be preserved at the time of sampling to a pH < 2 with hydrochloric acid. Drinking water compliance samples must be dechlorinated with ascorbic acid or sodium thiosulfate and preserved with hydrochloric acid to pH < 2 at the time of sampling. Drinking water compliance samples that are not preserved must be re-sampled and preserved before a valid analysis can be performed. If an unpreserved drinking water compliance sample is received, inform the Chemistry Technical Director immediately so that the proper notifications can be made.

5.4 Sample Storage

Samples must be stored at >0 and ≤ 6 °C. Retain samples for 60 days after the final analytical report is sent to the data user.

5.5 Holding Time

Acid preserved samples must be analyzed within 14 days from the date of sample collection; unpreserved samples must be analyzed within 7 days from the date of sample collection. See Section 5.3 regarding additional requirements for drinking water compliance samples.

Sort samples according to date sampled, so that samples can be analyzed in order of date sampled to prevent missed holding times.

6 INTERFERENCES

Method interference may be caused by impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, or solvent vapors in the laboratory. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory method and instrument blanks as described in Sections 8.3.2.1 and 8.3.2.2. The use of non-polytetrafluoroethylene (PTFE) tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and dichloromethane) through the septum seal into the sample during storage and handling.

Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the purging device and sampling syringe must be rinsed with reagent water between sample analyses. For samples containing large amounts of water-soluble materials, suspended solids, high-boiling compounds, or high purgeable levels, it may be necessary to wash out the purging device with methanol between analyses, rinse it with distilled water, and then dry it in an oven at 105°C. The trap and other parts of the system are also subjected to contamination; therefore, frequent bake out and purging of the entire system may be required.

Solvents and other compounds, which are target analytes must never be introduced into the laboratory where volatiles analysis is performed. Dichloromethane, acetone and other common laboratory chemicals are target analytes under this SOP and must be excluded from Room 201. Particular attention must be paid to the possibility of transport of solvent vapors on individuals. Analysts should never enter Room 201 after being in the extraction laboratories or glassware washing area.

7 APPARATUS AND MATERIALS

This section describes recommended apparatus and materials to be used for the analysis. All equipment, reagents, standards, and supplies must meet the technical and QC requirements of the reference method. Substitutions may be made provided that they are documented and equivalency is maintained.

7.1 Instruments and Equipment

- GCMS System

  Gas Chromatograph (GC): Hewlett Packard/Agilent 6890, 6890N, or 7890, or equivalent. The GC must be capable of multilevel temperature programming and constant carrier gas flow throughout the temperature range. The GC should be equipped with an automatic sample injector, split/splitless injection port, and electronic pressure control (EPC).

  Mass spectrometer: Hewlett Packard/Agilent 5973, 5973N, or 5975, or equivalent, capable of scanning from 35 to 300 amu every two second or less using 70 volts (nominal) electron energy in the electron impact ionization mode. The MS must be able to produce a mass spectrum that meets acceptance criteria when 25 ng of BFB is injected through the GC inlet.

  Column: Hewlett Packard HP-624 25M x 0.20 mm, 1.12 micron film, or equivalent. Any column capable of separating the target analytes and passing method QC without overloading at the concentration of the highest standard may be used.

- Data system: ChemStation (Agilent), or equivalent, able to control the GC/MS

system and to acquire, store, and reduce mass spectral data. The software must be able to process a GC/MS data file by recognizing a GC peak within a retention time window, comparing the mass spectrum from the GC peak with spectral data in a database, and generate a list of tentatively identified compounds with their retention times and scan numbers. The software must also allow integration of the ion abundance of any specific ion between specified time or scan number limits and to calculate RRFs and concentrations of analytes in samples.

- Purge and Trap Concentrator: Tekmar 3000, 3100, Stratum, EST Encon Evolution, or equivalent.
- Autosampler: Varian Archon, EST Centurion, or equivalent.

Other GC/MS systems with similar configurations can be used to analyze samples following this SOP as long as the instrumentation meets the requirements of this SOP.

7.2 Reagents

All chemicals must be entered into the Environmental Management System (EMS) upon receipt. Analysts must enter all reagents except organic-free method blank water into the LIMS.

Reagents may contain impurities that affect analytical data. Only materials that conform to the American Chemical Society (ACS) reagent grade specifications should be used. If the purity of a reagent is in question, analyze for contamination prior to use.

- Methanol (Purge and Trap grade).
- Reagent water: water in which method analytes or other interferences are at less than one-half the QL of the analytes of interest. Reagent water is prepared by bubbling contaminant-free inert gas through EPA Region 9 Laboratory deionized water. (Refer to EPA Region 9 Laboratory SOP 205 *Preparation of Organic-free Method Blank Water*.)
- Hydrochloric acid, (HCl) - analytical reagent grade
- Hydrochloric acid 1:1 (v/v), 1:1 HCl – carefully add a measured volume of concentrated HCl to an equal volume of organic-free reagent water and mix.

7.3 Standards

Standard solutions may be purchased as certified solutions or prepared from ACS reagent grade materials.

All standards must be entered into the Environmental Management System (EMS) upon receipt. The analyst must enter all standards into the LIMS. Standards are stored in designated refrigerators or freezers. Standards are not to be stored with samples. Protect all standards from light when stored.

Store ampulated standard solutions in the designated Room 201 refrigerator at >0° to ≤ 6°C. Follow manufacturer's recommendations for solution expiration date. Store all working standard solutions in glass bottles or vials with Teflon lined screw caps at ≤-10°C.

Several standard solutions contain peroxide-forming compounds such as acrylonitrile, diisopropyl ether, 1,1-dichloroethene, 1,4-dioxane, 4-methyl-2-pentanone, styrene, tetrahydrofuran, and vinyl chloride. Containers should be labeled with a peroxide-forming compound precautionary label. Discard dates and disposal instructions specified in USEPA Region 9 Laboratory SOP 785 *Procedures for Storage, Monitoring & Handling Peroxide forming Chemicals* must be followed.

7.3.1 General guidelines for preparation of diluted standards:

- All working standards must be prepared in clean, dry, volumetric flasks – see the tables in Section 7.3.2 for appropriate volumes.
- Add a volume of purge and trap grade methanol equal to at least one-half the total volume of the flask leaving sufficient volume to add all the solutions in the preparation.
- Use only gas-tight syringes in the volatiles laboratory. Triple rinse syringes with purge and trap grade methanol both prior to and after each use.
- Syringes should be selected to minimize measurement error. The percent error is high at the low end and it may be difficult to handle the syringe and plunger if it is used at full volume.
- Add the appropriate volume of each standard to the volumetric flask with the syringe needle beneath the surface of the methanol. Place the ground glass stopper on the flask between additions of standards.
- After adding the solutions indicated in the table, bring the volume to the mark with purge and trap grade methanol.
- Cap the volumetric flask with its ground glass stopper and gently invert the flask three times to assure mixing (do not shake).
- Pour the contents of the volumetric flask into a screw cap vial the same volume as the flask used for preparation, (or several smaller vials, but minimize headspace) equipped with a Teflon-lined screw cap and a Mininert valve.
- Do not use pipettes to transfer solutions containing volatile compounds because the vacuum used to draw the solutions up into the pipettes can cause some volatile compounds to come out of solution.
- All standards must be labeled with LIMS Standard ID, expiration date, analyst initials, and description.
- Expired or otherwise unusable standard solutions must be disposed in an appropriate waste container.

7.3.2 Working Standards:

- 4-Bromofluorobenzene Tuning Solution (BFB Solution, 50 ng/µL)

  Dilute 20 µL of a 5,000 ug/mL solution of 4-Bromofluorobenzene (VOA Tuning Compound solution, Restek catalog #30003 or equivalent) to 2 mL with purge and trap grade methanol.

  Replace the solution after 6 months, or sooner if analysis indicates that the tuning solution has degraded.

- Internal Standard / Surrogate solution (VOA IS/SS, 125 ng/µL)

  Dilute VOA IS/SS custom mix, Restek catalog #566692 or equivalent, as outlined in the following table.

Standards	Supplier	Conc., µg/mL	Amount, µL	Final Volume, mL	Final Conc. ng/µL
Custom IS Mix	Restek	10,000	125	10	125

  Fill a clean 5-mL standard reservoir and immediately install the standard reservoir in the appropriate standard position on the autosampler.

  Replace the solution after 14 days, or sooner if analysis indicates that the standard solution has degraded.

- Calibration mix (DW Mix, 25 - 200 ng/µL)

  Dilute the following standards, or equivalent, as outlined in the following table.

Standards	Supplier	Conc., µg/mL	Amount, µL	Final Volume, mL	Final Conc., ng/µL
502.2 Cal. Mix #1	Restek 30042	2,000	25	2	25
1,1,2-Trichloro-1,2,2-trifluoroethane	Restek 30462	2,000	25	2	25
VOA Calibration Mix 1 (ketones)	Restek 30006	5,000	80	2	200
1,2-Dibromo-3-chloropropane*	Restek 30270	2,000	75	2	100

Standards	Supplier	Conc., µg/mL	Amount, µL	Final Volume, mL	Final Conc., ng/µL
Carbon Disulfide	Restek 30258	2,000	25	2	25
Custom Ether/ THF Mix	Restek 30465	2,000	100	2	100
Restek Mega	Restek 30431	2,000	25	2	25

*1,2-Dibromo-3-chloropropane concentration includes 25 ng/µL from the 502.2 Cal Mix or the Mega Mix and 75 ng/µL from this standard.

Replace the solution after 7 days, or sooner if analysis indicates that the standard solution has degraded.

- Second Source Verification (SCV) Solution (DWLF solution, 25 - 500 ng/µL)

  Dilute the following standards, or equivalent, as outlined in the following table.

Standards	Supplier	Conc., µg/mL	Amount, µL	Final Volume, mL	Final Conc., ng/µL
502/524 VOC MIX	Supelco 5-02111	2,000	25	2	25
VOC MIX 6	Supelco 48799-U	2,000	25	2	25
VOA Calif. Oxygenates Mix	Supelco 4M6872-U	2,000-10,000	100	2	100-500
1,1,2-Trichloro-1,2,2-trifluoroethane	Supelco 4-7944	2,000	25	2	25
8240 Standard Mix 2	Supelco 47364	2,000	200	2	200
Carbon Disulfide	Supelco 40363	5,000	10	2	25

Replace the solution after 7 days, or sooner if analysis indicates that the standard solution has degraded.

7.4 Supplies

- Gas-tight syringes (5-µL, 10-µL, 25-µL, 50-µL, 100-µL, 250-µL, 500-µL, 1-mL, 5-mL, 25-mL and 50-mL).

- 25-mL fritted sparge vessels.
- Volumetric flasks, Class A - Appropriate sizes with ground glass stoppers
- pH paper (pH 0-14 range).
- Trap K (VOCARB 3000, EST EV1, or equivalent).
- VOA vials – pre-cleaned 40-mL glass vials equipped with screw-hollow caps lined with 22 mm PTFE-faced silicone septa.

8 ANALYTICAL PROCEDURES

8.1 Instrument Operation

Set-up the GC/MS following operating instructions provided by the manufacturer. Use operating parameters provided in Appendix D as a starting point.

Set-up the purge and trap following the operating parameters provided in Appendix D.

Ensure that appropriate waste containers are present and properly labeled.

Check the mass spectrometer for leaks on a daily basis prior to the analysis of the tuning check compound using the instructions provided in Appendix D.

8.1.1 Mass calibration

Mass calibration of the analytical system must be performed prior to an initial calibration, whenever the source is cleaned, or whenever a mass miss-assignment is noted. Mass calibration is performed to ensure the accurate assignment of masses to ions. Use perfluorotributylamine (FC43) to perform mass calibration of the instrument. Include the mass calibration printout with ICAL data.

Calibrate the mass axis of the MS prior to analyzing the BFB solution each day that samples are analyzed. Use the settings in the most recent tune file as the initial conditions; save the tune file using the naming convention in Appendix E, and generate a tune report. Include the mass calibration printout with analysis data.

8.1.2 GC/MS Tuning Check

The GC/MS system must meet the mass spectral ion abundance criteria for BFB prior to analysis. Proper tuning of the instrument is necessary to produce standardized fragmentation patterns of target compounds.

Inject 0.5 µL of a 50 ng/µL BFB solution using the operating parameters provided in Appendix D. Optionally, purge BFB in water solution. Prepare this solution by

adding 1 µL of a 50 ng /µL BFB solution to a 50-mL syringe filled with acidified reagent water and decant into a 40-mL vial as shown in Appendix D.

Evaluate BFB in Chemstation by selecting "Tuner", "Evaluate BFB". The autofind procedure will automatically find the BFB peak, average three scans (the peak apex scan and the scans immediately preceding and following the apex), perform a background subtraction, and print out a hard copy of the spectrum, the chromatogram, and the table of ion abundances. Follow requirements and take corrective action as described in Section 9.2.1.

Refer to Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.2 Calibration and Standardization

8.2.1 Initial Calibration

Perform an initial calibration. Prepare standards at the following recommended concentrations:

Calibration Standard Amounts for 50 mL Final Volume

Calibration Level	Concentration, µg/L	VOA IS/SS* Mix 125 µg/mL, µL	DW Mix 25 µg/mL, µL
1	25	1	50
2	10	1	20
3**	5	1	10
4	2	1	4
5	1	1	2
6***	0.5	1	1

* Added by the autosampler.
** CCV, LCS, MS, MSD concentrations except as noted below.
*** LCV/MRL/QLS concentrations except as noted below. Do not vary the concentration.

NOTE: Since ketones, ethers, and 1,2-dibromo-3-choropropane purge poorly from aqueous samples, they are analyzed at higher concentration ranges. See Section 7.3.2 for recommended concentrations.

Check the initial calibration for misidentified peaks due to retention time shifts. The most commonly misassigned compounds are the 1,3- and 1,4-dichlorobenzenes.

No quantitation ion may saturate the detector; review the 25 µg/L calibration standard (or the highest concentration included in the initial calibration) to confirm that this criterion is met.

The data system calculates the relative response factor (RRF) for each target compound and surrogate compound for all calibration standards using the following equation. The quantitation ions and internal standard assignments are listed in Appendix C.

$$RRF = (Ax)(Cis) / (Ais)(Cx)$$

Where

Ax = Area of quantitation ion of compound x
Ais = Area of quantitation ion for associated internal standard
Cx = Concentration of compound x
Cis = Concentration of the associated internal standard

The data system calculates the percent relative standard deviation (%RSD) of the RRF values for each compound using the following equation.

$$\%RSD = (SD/ RRF_{avg})*100$$

Where

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(x_i - x_{ave})^2}{n-1}}$$

RRF_{avg} = Average Relative Response Factor from the ICAL

Analyze a SCV at standard level 3 outlined in Section 8.2.1. The SCV is prepared in the same manner as the CCV except it is spiked with the Second Source Verification (SCV) Solution (DWLF solution, 25 ng/µL, ketones 200 ng/µL).

Refer to Appendix D for ChemStation calculation and calibration instructions.

Refer to Section 9.2.2 and Appendix C for acceptance criteria and corrective action requirements.

8.2.2 Continuing Calibration Verification (CCV)

Perform continuing calibration using the recommended concentration outlined in Section 8.2.1.

The data system calculates the percent deviation (%D) of the RF values for each compound using the following equation:

$$\%D = \frac{RRF_c - RRF_{avg}}{RRF_{avg}} x\ 100$$

Where:
RRF_C: Relative Response Factor of compound in the CCV.
RRF_{avg}: Average Relative Response Factor from the ICAL.

Refer to Appendix D for ChemStation calculation and calibration instructions.

Refer to Section 9.2.3 and Appendix C for acceptance criteria and corrective action requirements.

8.2.3 Closing Calibration Verification

When analyzing drinking water compliance samples, analyze a closing calibration verification using the recommended continuing calibration concentration level outlined in Section 8.2.1.

Refer to Section 9.2.4 and Appendix C for acceptance criteria and corrective action requirements.

8.2.4 Low Level Calibration Verification (LCV) or Quantitation Limit Standard (QLS)

Analyze the low level calibration verification using the recommended concentration outlined in Section 8.2.1.

The LCV concentrations match the QL concentration (at the instrument). The recovery of analytes in the LCV is calculated as:

$$\%R = \frac{M}{T} \times 100$$

Where

%R	=	percent recovery of the standard.
M	=	measured concentration of the analyte, ug/L.
T	=	true concentration of the analyte in the ug/L.

Refer to Section 9.2.5 and Appendix C for acceptance criteria and corrective action requirements.

8.3 Analysis

8.3.1 Sample Preparation

Allow the sample to reach ambient temperature before analysis.

Verify that the sample identification on the vials coincides with the sample identification on the COC and the LIMS to ensure that the correct sample is being analyzed.

Check if the sample has an unusual color or other physical properties. If any physical signs of contamination are present, screen the sample to protect the analytical system from damage or contamination, and to determine the appropriate subsequent dilutions. Record unusual items in the LIMS work order memo field.

Note: After the analysis is complete, check the pH for each sample using pH 0-14 range pH paper. If samples are drinking water compliance, check the residual chlorine in each sample using chlorine test strips. Record the results in LIMS. If any sample has a pH greater than 2 or if a drinking water sample has residual chlorine, make a note in the LIMS work order memo field. Contact the Chemistry Team Leader who will follow up to determine if resampling is required.

8.3.2 Sample Analysis and Analytical Sequence

This section describes preparing the analytical sequence and analyzing the samples.

Make a LIMS batch containing the samples to be analyzed and an empty LIMS sequence to obtain LIMS assigned IDs for the instrument and batch QC samples.

Document sample dilutions by entering the initial/final volumes in the LIMS bench sheet.

Prepare all instrument and batch QC samples in acidified reagent water.

To spike the MS and MSD, quickly remove the 40-mL sample vial cap from each vial and spike directly in the field sample vial and recap the vial.

Prepare the samples to be analyzed. The following table represents the spike levels recommended for most projects:

Spike Amounts

Sample	VOA IS/SS Mix* 125 µg/mL, µL*	DW Mix 25 µg/mL, µL
Blanks	1.0	NA
Samples	1.0	NA
BS/LCS	1.0	10.0

MS/MSD	1.0	8.0

Prepare LCS in 50-mL volumetric flask and transfer to 40-mL vial.
NA = Not Applicable
* IS/SS is added by autosampler.

Load the samples in the autosampler according to their designated positions in the sequence file. The following represents a recommended analysis sequence:

1. BFB
2. CCV/LCS*
3. LCV (QLS)
4. MB
5. Samples
6. MS/MSD, as needed**
7. Sample dilutions, as needed
8. Storage Blanks and Instrument Blanks, as needed

* CCV and LCS requirements may be satisfied in one analysis.
** When included, analyze MS/MSD and source sample early in the sequence to allow QC review prior to completion of the sequence, if possible.

Gently place the vial in the appropriate autosampler position.

Enter sample sequence in the instrument software. Include the LIMS sample number (WO-sample number) in the "Sample" field.

Name the data files according to the data file naming convention outlined in Appendix E.

8.3.2.1 Method Blank

Prepare method blanks by filling a 40-mL screw-capped volatile vial fitted with a PTFE-faced silicone septum with acidified organic-free method blank water.

See Section 9.3.1 for frequency, acceptance criteria, and corrective action requirements.

The method blank is acceptable if it meets criteria listed in Appendix C.

8.3.2.2 Instrument Blank

As needed, prepare instrument blanks in the same manner as method blanks.

See Section 9.3.2 for acceptance criteria and corrective action requirements.

Note: The instrument blanks may be analyzed beyond the 12 hour tune time period.

8.3.2.3 Storage Blank

Prepare storage blanks as described in Section 9.3.3.

See Section 9.3.3 for frequency, acceptance criteria, and corrective action.

Note: The storage blanks may be analyzed beyond the 12 hour tune time period.

8.3.3 Analyte Identification and Quantitation

8.3.3.1 Analyte Identification

For a target analyte to be identified as present in a sample both the retention time and the mass spectra of the peak must match those of the standard.

This SOP specifies the use of NIST library spectra as reference spectra to prevent confusion due to co-elution of compounds in the calibration standards. Therefore, do not update the reference spectra in the method.

All ions present in the NIST mass spectra at a relative intensity of 10 % of the most abundant ion must be present in the sample spectra.

The relative intensities of the ions must agree within 20 % between sample spectra and the CCV level spectra of the most recent ICAL.

Ions present in the sample but not present in the standard spectra should be reviewed for possible coelution.

If a compound cannot be verified consistent with these criteria but, in the technical judgment of the analyst, is present, the analyte is reported and supporting evidence must be noted on the raw data.

8.3.3.2 Analyte Quantitation

Quantitate the data and print out a quantitation report and chromatogram for each sample. Use the average relative response factor from the initial calibration for quantitation.

8.3.4 Calculations

Target analyte concentrations as shown on the ChemStation quantitation report are calculated using the following equation:

Conc. (µg/L) = Ax * AMTIS * DF / (AIS * RRF)

Where:

Ax	= area of the quantitation ion of the compound
AMTIS	= amount of internal standard in µg/L (5 µg/L)
DF	= dilution factor
AIS	= area of the characteristic ion of the associated internal standard
RRF	= analyte average relative response factor from the initial calibration

LIMS calculates the final analyte concentration in samples from the result in the ChemStation quantitation report and the initial and final volumes in the LIMS bench sheet.

8.3.4.1 Manual Integration

Where the chromatography software integrates the signal inconsistently, follow EPA Region 9 Laboratory SOP 835 *Chromatographic Integration Procedures*. All manual chromatographic integration must be initialed and dated by the analyst and approved by the supervisor, Chemistry Technical Director, Quality Assurance Officer, or designees.

8.3.5 Review of Tentatively Identified Compounds:

The TICs reporting requirement is determined by the Technical Director on a project by project basis and noted in the LIMS project or work order memo fields. Check project requirements before reviewing data.

Load the data file of the most concentrated valid analysis of the sample.

Review the library search results for the following:

Check that each significant peak in the LSC Report has been reported either in the ChemStation quantitation report or the LSC report.

Report those TICs for which the response is greater than 20% of the closest internal standard.

Use the nearest internal standard free of interferences for quantitation.

Report up to 10 TICs based on largest total area.

Relative intensities of the major ions in the NIST reference spectrum (ions greater than 10 % of the most abundant ion) should be present in the sample spectrum.

The relative intensities of the major ions should agree within 20 %.

Molecular ions present in the reference spectrum should be present in the sample spectrum.

Ions present in the sample spectrum but not in the reference spectrum shall be reviewed for possible background contamination or the presence of co-eluting compounds.

Ions present in the reference spectrum but not within the scan range of the method should not be considered when making a tentative identification.

If, in the technical judgment of the analyst, no valid tentative identification of the compound can be made, the compound should be reported as "Unknown"; attempt to classify the unknown compound (i.e., unknown hydrocarbon, unknown aromatic, unknown chlorinated compound, etc.).

Report the following:

a. Class of compound instead of specific isomers unless the identity of the specific isomer is known. As an example, report dichlorobenzene instead of 1,2-dichlorobenzene. Alternatively, report 1-methylnaphthlene if the calibration standard has 2-methylnaphtalene and the TIC retention time is not that of 2-methylnaphtalene. Edit the TIC name to correct errors and remove extraneous punctuation.

b. Total of all hydrocarbons as "Total Hydrocarbon", if required, is determine as follows:
   - Click "Int" and make sure that "integrate a peak" option is not selected.
   - Click and hold the left mouse button and drag the cursor across the entire hydrocarbon peak range; this will generate an average spectrum of the range.
   - Determine whether m/z 55 or 57 is larger in the spectrum. Click "Int", "Ion Chromatogram" and enter the larger of the two ions (55 or 57).
   - Click "Int" and select "integrate a peak" then integrate the hydrocarbon peak range.

- Click "File", "Print Trace + spectrum". Click "Int", "Integration Results", "Print"; this prints the area for the total hydrocarbon peak.
- Calculate the estimated total hydrocarbon concentration by dividing the area of the total hydrocarbon peak determined above by the area of the closest IS to the center of the total hydrocarbon peak from the quantitation report (not the LSC report) then multiplying this result by the concentration of the IS.
- Click "LSC", "LSC for current scan"; this adds the peak to the LSC report.
- Click "LSC", "Edit LSC Results". Select "unknown hydrocarbon" and change name to "Total Hydrocarbon" then enter the concentration of the total hydrocarbon peak determined above.

Exclude the following compounds from the report:

a. Analytes eluting prior to the first eluting target compound in the CCV.
b. TICs that were detected in the method blank.
c. Column bleed (i.e. siloxanes).
d. CO2/fixed gases peak.
e. Electronic noise peaks.

If the base peak saturates the detector, document this in the data. Do not dilute a sample to get the base peak of a TIC within the detector range. If a sample containing a saturated TIC ion was diluted to get a target compound within calibration range, use the TIC base peak area from the diluted analysis to estimate the concentration of the TIC.

8.3.6 Data and QC Review

As soon as possible after analysis (typically prior to entry into LIMS), inspect sample and QC data for compliance with QC limits in Appendix C. If no significant problems are found, perform the following QC reviews for compliance with SOP requirements:

- Process and review the results for the CCV and instrument QC samples. Print a ChemStation Evaluate Continuing Calibration Report using the appropriate settings to verify that the CCV and LCV (QLS) results are within QC limits. See Section 9.2 for instrument QC requirements.

- Process and review the results for the MB, LCS, and MS/MSD and batch QC samples and verify that the results are within QC limits. See Section 9.3 for batch QC requirements.

- Print a ChemStation QA-QC Check Report after processing all the samples.

- Check the sample's surrogate and internal standard recoveries with criteria in Appendix C.
- Determine if surrogate recoveries for field and QC samples are within QC limits. See Section 9.4 for Sample QC requirements.
- Review all sample results to determine if any samples need to be re-analyzed at a dilution.
- Review the chromatogram for possible false negatives.
- Manually cross out and initial all compounds that do not meet qualitative criteria and document the reason on the quantitation report. Delete the compound (Qdel) in ChemStation.
- If a run is rejected for any reason, mark the raw data "Not Used" in large print and document the reason on the quantitation report.

8.3.7 Data Export and LIMS Entry

Generate epatemp.txt files for field and QC samples by printing the report to the screen; these files are used by the LIMS DataTool module to import the instrument results into the Data Entry/Review table and to populate the empty LIMS sequence.

Copy sample data files from the local drive to the appropriate instrument data subdirectory on the Region 9 LAN to make them available to LIMS and to archive them.

Populate the empty LIMS sequence with the samples actually analyzed by editing the empty LIMS sequence; import the sample information using DataTool.

Create an empty upload file containing the samples analyzed in the LIMS batch or sequence. Import and merge the data files using the LIMS DataTool module. Load the resulting merged data file into the LIMS Data Entry/Review table. See the LIMS manual for detailed procedure.

Review results in the LIMS. Qualify and flag results in the LIMS Data Entry/Review table following Appendix R of the Region 9 Laboratory Quality Assurance Manual.

8.4 Maintenance:

The analyst should observe trends in the data such as declining response, erratic relative

response, loss of classes of compounds, etc., which may signal the need for instrument maintenance. Document all routine maintenance or corrective actions taken in the maintenance logbook. Routine maintenance procedures and frequency are listed in Appendix F.

8.4.1 Purge and trap maintenance

Symptom:

- Decline in chloromethane, bromomethane, chloroethane, bromoform, and / or 1,2-dibromo-3-chloropropane responses.

  Cause: purge flow rate or trap problem.
  Corrective action: Check purge flow; replace trap if necessary.

- Carryover of naphthalene and/or 1,2,3-trichlorobenzene

  Possible causes: Cold spot in system, especially the transfer lines between the sparge unit and the concentrator or between the concentrator and the GC or analyzing a sample containing high mole weight components or analyzing high-level and low-level samples sequentially.

  Corrective action: Check temperatures of all heated zones. Adjust temperatures or replace heaters as required. Flush valve, gas lines, and sample lines with methanol or reagent water and bake out.

- Loss of sensitivity to selected analytes and increased pressure to maintain purge flow.

  Possible cause: Degradation of trap.
  Corrective action: Replace trap.

- Loss of all purged analytes.

  Possible cause: Leak in system.

Corrective action: Leak check purge and trap system. Inspect sparge ferrules and replace them when worn or distorted.

8.4.2 GC Maintenance

Symptom

- Carryover

Possible causes: Analyzing a sample containing high mole weight components or analyzing high-level and low-level samples sequentially.

Corrective action: As necessary, replace inlet liner, clean inlet, bake out inlet, bake out column, clip column, replace septum, replace column.

- Shorter retention time.

  Possible cause: column flow rate problem.

  Corrective action: check flow rate and adjust as necessary.

- Longer retention time and or smaller peaks.

  Possible causes: column flow rate problem, injection port leak, or column contamination.

  Corrective action: As necessary, check for leaks, replace septum, replace the liner, replace the lower injection port seal, and cut the column (a few inches to a foot or more) from the injector end. If issues remain, replace the column.

- Loss of resolution or tailing.

  Possible causes: column flow rate problem, injection port leak, or column contamination.

  Corrective action: Check for leaks, replace septum, replace the liner, replace inlet seal, and clip the column (a few inches to a foot or more) from the injector end. If issues remain, replace the column.

8.4.3 MS maintenance:

Trend to be observed:

- Low m/z 502 to 69 ratio
- Failing tune checks

Corrective action: Clean the source.

9 QUALITY CONTROL

The EPA Region 9 Laboratory operates a formal quality control program and tracks compliance using the Lab QC Database. As it relates to this SOP, the QC program consists

of a demonstration of capability, and the periodic analysis of MB, LCS, and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated. A summary of QC criteria is provided in Appendix C.

9.1 Demonstration of Capability

A demonstration of capability (DOC) must be in place prior to using an analytical procedure and repeated if there is a change in instrument type, personnel, or method. Follow procedures described in EPA Region 9 Laboratory SOP 880 *Demonstration of Capability*.

9.2 Instrument QC

9.2.1 GC/MS System Performance Check (BFB analysis):

The GC/MS system must meet the mass spectral ion abundance criteria for BFB prior to analysis.

If the ion abundances fail to meet criteria listed in Appendix C, the BFB chromatogram should be examined for any obvious chromatographic problems (e.g. bad injection leading to poor response etc.). If the problem is determined to be related to poor chromatography take the necessary corrective action and re-analyze the BFB. If the BFB continues to fail the ion abundance criteria retune the mass spectrometer, it may be necessary to clean the ion source, or take other corrective action to achieve the ion abundance criteria.

If a sample is injected after the BFB time period has elapsed it must be re-analyzed.

9.2.2 Initial Calibration

Each GC/MS system must be calibrated whenever corrective action is performed which may change instrument response (e.g., ion source cleaning, column replacement, etc.) or if the continuing calibration acceptance criteria cannot be met.

If an ICAL fails because of one standard, a fresh solution of that standard may be re-analyzed once and substituted for the standard that failed in the ICAL. If the failure is repeated (or the problem is not isolated to one calibration point), the system must be repaired so that criteria are satisfied.

Qualify and flag results in the LIMS Data Entry/Review table following Appendix R of the Region 9 Quality Assurance Manual.

If the calibration does not meet the SCV criteria listed in Appendix C, the SCV may be re-analyzed once. If the failure is repeated, terminate the analysis, correct the problem, and prepare a new calibration curve.

9.2.3 Continuing Calibration Verification

Examine the areas of the quantitation ions of the internal standards in the calibration verification standard.

Examine the retention time of the internal standards in the calibration verification standard.

Qualify and flag results in the LIMS Data Entry/Review table following Appendix R of the Region 9 Quality Assurance Manual.

If the continuing calibration does not meet %D criteria listed in Appendix C, the CCV may be re-analyzed once. If the failure is repeated, the analysis shall be terminated, the problem corrected, documented, and two consecutive successful CCVs or a new initial calibration analyzed.

9.2.4 Closing Continuing Calibration Verification – required when analyzing drinking water compliance samples

Examine the areas of the quantitation ions of the internal standards in the calibration verification standard.

Examine the retention time of the internal standards in the calibration verification standard.

Qualify and flag results in the LIMS Data Entry/Review table following Appendix R of the Region 9 Quality Assurance Manual.

If the continuing calibration does not meet %D criteria listed in Appendix C, the closing CCV may be re-analyzed once. If the failure is repeated, drinking water compliance samples must be reanalyzed in a sequence with an acceptable closing CCV.

9.2.5 Low Level Calibration Verification (Quantitation Limit Standard)

A LCV (QLS) must be analyzed at the beginning of the analytical sequence (typically after the CCV/LCS).

Generate a LCV (QLS) report and check that the recoveries meet criteria specified in Appendix C.
Qualify and flag results in the LIMS Data Entry/Review table following

Appendix R of the Region 9 Quality Assurance Manual.

If the LCV (QLS) recovery does not meet criteria provided in Appendix C, rerun the LCV (QLS) once to verify. If still unacceptable, determine the cause and take corrective action.

9.3 Batch QC

9.3.1 Method Blank

A method blank must be analyzed at the beginning of the analytical sequence (typically before samples are analyzed).

If a method blank fails to meet criteria, use the following guidelines to determine when samples must be re-analyzed:

a) If the MB analyte value ≥½ QL and the sample result is less than five times the MB analyte amount, all associated samples containing less than five times the MB analyte amount may have to be re-analyzed. Consult with the Chemistry Technical Director or designee. Common laboratory contaminants (acetone, dichloromethane) are excluded; flag the results for these analytes following Appendix R of the Region 9 Laboratory Quality Assurance Manual.

b) If the MB analyte value ≥½ QL and the sample result is greater than five times the MB analyte concentration or is non-detected, report sample result.

9.3.2 Instrument Blank and high concentration samples

In the event that a known high concentration sample containing analytes which exceed the calibration range of the instrument is analyzed, analyze an instrument blank to demonstrate that the system is free of carryover contamination. If a high concentration sample was analyzed in the absence of an IB, the analyst must evaluate any sample that is analyzed immediately following the overrange sample to determine if carryover may have occurred.

Use the following guidelines when instrument blank data is available:

a) If the IB analyte value ≥½ QL and the sample result is less than five times the IB analyte amount, re-analyze the sample if an additional aliquot is available. If re-analysis is not possible, flag sample result following Appendix R of the Region 9 Laboratory Quality Assurance Manual.

b) If the IB analyte value ≥½ QL and the sample result is greater than five times the IB analyte concentration, report sample result.

In the absence of an instrument blank, the subsequent sample result must be evaluated for potential contribution by the overrange sample. If the analyte value ≥½ QL, re-analyze the sample if an additional aliquot is available. If re-analysis is not possible, flag sample result following Appendix R of the Region 9 Laboratory Quality Assurance Manual.

9.3.3 Storage Blank (SB)

Every Monday morning, or the first work day of the week, fill two 40-mL screw-cap volatile vials with PTFE-faced silicone septa with acidified organic-free method blank water and store them with the samples in the sample storage refrigerator in Room 201.

Analyze the storage blank, prepared and stored last week, on the first workday of the week.

Use the following guidelines if contamination is present:

a) If the SB analyte value ≥½ QL and the sample result is ≥½ QL but less than five times the SB analyte amount, flag sample result.

b) If the SB analyte value ≥½ QL and the sample result is non-detected or greater than five times the SB analyte concentration, report sample result unflagged.

9.3.4 LCS

Since the CCV and LCS are prepared from the same source and at the same concentration, one analysis serves both purposes. However, LCS acceptance criteria are determined from historical data.

Using the same file as the passing CCV, calculate LCS recovery:

$$\%R = \frac{Cm}{Ct} \times 100$$

Where

$\%R$	=	percent recovery.
Cm	=	measured analyte concentration in the LCS.
Ct	=	true analyte concentration in the LCS.

Generate an LCS report and check that the recoveries meet criteria specified in Appendix C.

If the LCS recovery does not meet criteria provided in Appendix C, rerun the LCS

once to verify. If still unacceptable determine the cause, take corrective action and document these actions. Samples may not be analyzed without an acceptable LCS unless an approved discrepancy is obtained prior to continuing the analysis (see EPA Region 9 Laboratory SOP 820 *Laboratory Discrepancies and Corrective Actions*).

In the LIMS Data Entry/Review table, qualify and flag results associated with outliers following Appendix R of the Region 9 Laboratory Quality Assurance Plan.

9.3.5 Matrix Spike/Matrix Spike Duplicate

The MS and MSD are designed to provide information about the affect of sample matrix on the measurement system. One set of MS/MSD samples must be analyzed for each SDG. Do not evaluate MS/MSD recovery for any analyte whose concentration in the MS/MSD source sample is more than four times the MS/MSD spike level. Do not evaluate MS/MSD recovery for any analyte exceeding the calibration range of the instrument.

Samples identified as field blanks or trip blanks cannot be used for MS/MSD sample analysis.

MS/MSD recoveries are calculated as:

$$\%R = \frac{Cms - C}{s} \times 100$$

Where

$\%R$ = percent recovery.

C_{ms} = measured concentration of analyte in the MS, corrected for sample preparation and any dilutions.

C = measured concentration of analyte in the routine sample corrected for sample preparation and any dilutions.

s = expected analyte concentration in the MS, corrected for sample preparation and any dilutions.

Calculate the relative percent difference (RPD) using the following equation:

$$RPD = \frac{|Cmsd - Cms|}{(Cmsd + Cms)/2} \times 100$$

Where

RPD = relative percent difference.

C_{msd} = measured concentration in the MSD, corrected for sample preparation and any dilutions.

C_{ms} = measured concentration in the MS, corrected for sample preparation and any dilutions.

If the MS/MSD analytes do not meet these criteria, examine other QC results to determine if a matrix problem exists. If laboratory performance is in control, the poor MS accuracy or precision is likely to be matrix-related.

Flag results in the LIMS Data Entry/Review table following Appendix R of the Region 9 Laboratory Quality Assurance Plan.

- The table below lists the action to be taken based on the LCS and MS/MSD results.

QC ACCEPTANCE MATRIX + = PASS								**! = FAIL**
CASE	1	2	3	4	5	6	7	8
LCS - % REC	+	+	+	+	–	–	–	–
MS/MSD -% REC	+	–	+	–	+	–	+	–
MS/MSD – RPD	+	+	–	–	+	+	–	–

Case 1: Batch acceptable.
Case 2: Batch acceptable; matrix effect confirmed.
Cases 3 & 4: Batch is unsatisfactory. Investigate MS/MSD problem and document findings in the LIMS work order memo field.
Cases 5, 6, 7, & 8: Batch rejected. If additional sample volume is available, the batch should be re-analyzed.

9.4 Sample QC

9.4.1 Surrogate Recovery

Check the surrogate recovery in all field and QC samples immediately after analysis.

ChemStation calculates the surrogate recovery using the following formula:

Equation 9:

$$\%R = (\text{Amount Found}/\text{Amount Spiked}) \times 100.$$

The surrogate recovery must be within QC limits outlined in Appendix C.

Take the following steps if surrogate recovery is not within the limits:

1. Ensure that there are no calculation errors, and check the system performance.
2. Re-analyze the sample if a system performance problem or calculation error is not evident. The sample may be diluted for re-analysis if examination of the chromatogram so indicates.

Do not reanalyze undiluted samples with surrogate recoveries outside the limits if the diluted analysis with acceptable surrogate recoveries is being submitted. Report the event in the runlog.

Do not re-analyze the MS/MSD samples, even if surrogate recoveries are outside the limits.

If the sample associated with the MS/MSD analyses does not meet the surrogate recovery criteria, it should be re-analyzed only if the matrix spike and duplicate surrogate recoveries meet criteria. If the sample and spikes show the same pattern (i.e., outside the limits), then sample reanalysis is not required.

If surrogate recoveries of the re-analysis are within limits, the problem is assumed to have been within the laboratory's control. Report the results from the re-analysis and submit data for both analyses. Distinguish between the analysis and re-analysis by adding an "RE" suffix to the sample ID on the re-analysis. The problem must be documented in the LIMS work order memo field.

If the re-analysis fails to meet criteria, report the results from the first analysis and submit the data for both analyses. Distinguish between the original analysis and the re-analysis by adding the "RE" suffix to the sample ID in the re-analysis.

9.4.2 Internal Standard Area:

Evaluate the internal standard areas in all field and QC samples immediately after analysis.

The internal standard areas must be within QC limits outlined in Appendix C.

Take the following steps if the internal standard areas do not meet criteria:

1. Check the system performance.
2. Re-analyze the sample if a system performance problem is not evident. The sample may be diluted for re-analysis if examination of the chromatogram so indicates.

Do not reanalyze undiluted samples with internal standard areas outside the limits if the diluted analysis with acceptable internal standard areas is being submitted.

Do not re-analyze the MS/MSD samples, even if internal standard areas are outside the limits.

If the sample associated with the MS/MSD analyses does not meet the internal standard areas criteria, it should be re-analyzed only if the matrix spike and duplicate internal standard areas are within the limits. If the sample and spikes show the same pattern (i.e., outside the limits), then the sample does not need re-analysis.

If the internal standard areas are of the re-analysis are within limits, the problem was within the laboratory's control. Report the results from the re-analysis and submit the data from both analyses. Distinguish between the analysis and re-analysis by adding an "RE" suffix to the sample ID on the re-analysis. The problem must be documented in the LIMS work order memo field.

If the re-analysis does not solve the problem, report the results from the first analysis and submit the data from both analyses. Distinguish between the original analysis and the re-analysis by adding the "RE" suffix to the sample ID in the re-analysis.

9.5 Method Performance

Refer to the table in Appendix G for a summary of method performance at the 95% confidence level (2σ). Data are from the Region 9 Laboratory for water samples analyzed from September 7, 2012 to February 11, 2013.

Functional areas of the SOP that may be significant sources of analytical error are:

1. Sample handling. Loss of volatile compounds due to excessive sample handling.
2. Sample volatilization and degradation. Samples must be stored as outlined in the SOP to minimize losses.
3. Sample temperature: Samples must be allowed to come up to room temperature prior to analysis. Failure to do so will cause heavy molecular weight analytes to precipitate thus reducing the observed concentration.
4. Poor column condition may results in inadequate analyte separation and inaccurate integration.
5. Trap condition.
6. Leaks in sample transfer and GC/MS systems.

10 DOCUMENTATION

10.1 Standards

All standards (ICAL, SCV, CCV/LCS, LCV (QLS), and MS/MSD) are recorded in the

LIMS. A copy of each Analytical Standard Record associated with sample analysis must be included in the data package.

10.2 Reagents

Record all reagents used for each analytical batch in the LIMS and on the benchsheet.

10.3 Analytical Sequence

The analytical sequence is documented in the Element database or in the instrument Run Log, date of analysis, QC solution IDs, analyst initials, lab sample IDs, dilution factors and comments, if any, are recorded.

10.4 Analytical Report and Data Package

Analytical reports are produced using the LIMS. The data package is produced from LIMS and manual log records. EPA Region 9 Laboratory SOP 845 *Analytical Data Review* provides the typical format for data package deliverables.

10.5 Maintenance Logbook

Maintain a maintenance logbook for each instrument covered in this SOP. Document the following:

- Initial installation and performance
- Subsequent instrument modifications and upgrades, including major software upgrades
- All preventive or routine maintenance performed including repairs and corrective or remedial actions. Whenever corrective action is taken, record the date, the problem and resolution, and documentation of return to control.

All entries should be made in accordance with EPA Region 9 Laboratory SOP 840, *Notebook Documentation and Control.*

10.6 SOP Distribution and Acknowledgement

After approval, distribute an electronic copy of the final SOP to all laboratory staff expected to perform the SOP or review data generated by the SOP. (The Lab QC Database contains a list of assigned analysts for each SOP). All approved EPA Region 9 Laboratory SOPs are maintained in the LotusNotes database in Adobe Acrobat portable document format.

Analyst training is documented via the Training Record form and the Read and Understood Signature log; the latter is entered into the Lab QC Database.

10.7 SOP Revisions

Revisions to this SOP are summarized in Appendix H.

11 REFERENCES

EPA Region Laboratory documents (SOPs, the Laboratory Quality Assurance Plan, etc.) are not included in this list. Analysts are referred to the SOP database on LotusNotes, laboratory users should contact the Chemistry Team Leader or Laboratory QAO for copies of any supporting documents.

Agilent Technologies EnviroQuant ChemStation User's Guide.

Agilent Technologies/HP 5973 GC/MS Users Manual.

Agilent Technologies 5975 GC/MS Users Manual.

EST Analytical Manuals (Centurion, Cobra L-S, Encon Evolution, HS9000, LC-241 Plus, and LGX50).

Varian Archon Autosampler and HP/Archon/Tekmar Concentrator Operator's Manuals.

U.S. Environmental Protection Agency, 1995. Method 524.2, *Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, Revision 4.1.*

USEPA Method 5035A, *Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples*; Draft Revision 1, July 2002.

USEPA Method 8000C, *Determinative Chromatographic Separations*; Revision 3, March 2003.

USEPA Method 8260B, *Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry: Capillary Column Technique*; Revision 2, December 1996.

APPENDIX A.
DEVIATIONS FROM THE REFERENCE METHOD

1. This SOP follows the Region 9 Laboratory Quality Assurance Plan which specifies preservation and storage temperatures of >0° to ≤ 6°C, while the reference method specifies < 4°C.

2. The reference method specifies using m/z ion 95 as the quantitation ion for 4-bromofluorobenzene. The Region 9 Laboratory uses m/z ion 174 for quantitation of 4-bromofluorobenzene to avoid possible interference from a target analyte.

3. Section 11.6 of Method 524.2 describes using the spectra generated by the analytical system as reference spectra for target analyte identification. This SOP specifies the use of NIST library spectra as reference spectra to prevent confusion due to co-elution of compounds in the calibration standards.

3. This procedure uses QC limits generated from Region 9 Laboratory data. Deviations are allowed for up to 10% of these limits. This allowance is not included in the reference method.

4. The three standard deviations of the mean retention time is not evaluated in this SOP as discussed in Method 524.2. ChemStation calculates an absolute retention time difference for sample components, not SD difference. A retention time window of ± 0.5 min is used in this SOP.

APPENDIX B.
ANALYTES AND QUANTITATION LIMITS

The following table contains target compounds and quantitation limits covered by this SOP. Routinely reported analytes are indicated; other listed compounds may be added on a project-specific basis. When required, lower quantitation limits may be reported when supported by method detection limit studies and appropriate QC and calibrations are performed. Analytes regulated under the Safe Drinking Water Act are identified.

Compound Name	CAS No.	QL, ug/L	Regulated	Routinely Report
Dichlorodifluoromethane	75-71-8	0.5		X
Chloromethane	74-87-3	0.5		X
Vinyl chloride	75-01-4	0.5	X	X
Bromomethane	74-83-9	0.5		X
Chloroethane	75-00-3	0.5		X
Trichlorofluoromethane	75-69-4	0.5		X
1,1-Dichloroethene	75-35-4	0.5	X	X
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)	76-13-1	0.5		X
Acetone	67-64-1	4.0		X
Carbon disulfide	75-15-0	0.5		
Dichloromethane	75-09-2	0.5	X	X
tert-Butyl alcohol	75-65-0	10		
trans-1,2-Dichloroethene	156-60-5	0.5	X	X
tert-Butyl methyl ether (MTBE)	1634-04-4	2.0		X
1,1-Dichloroethane	75-34-3	0.5		X
Diisopropyl ether	108-20-3	2.0		
Ethyl *tert*-butyl ether	637-92-3	2.0		
2,2-Dichloropropane	594-20-7	0.5		X
cis-1,2-Dichloroethene	156-59-2	0.5	X	X
2-Butanone (MEK)	78-93-3	4.0		X
Bromochloromethane	74-97-5	0.5		X
Chloroform*	67-66-3	0.5	X	X
1,1,1-Trichloroethane	71-55-6	0.5	X	X
tert-Amyl methyl ether	994-05-8	2.0		
1,1-Dichloropropene	563-58-6	0.5		X
Benzene	71-43-2	0.5	X	X
1,2-Dichloroethane	107-06-2	0.5	X	X
Carbon tetrachloride	56-23-5	0.5	X	X
Trichloroethene	79-01-6	0.5	X	X
1,2-Dichloropropane	78-87-5	0.5	X	X
Dibromomethane	74-95-3	0.5		X
Bromodichloromethane*	75-27-4	0.5	X	X
cis-1,3-Dichloropropene	10061-01-5	0.5		X
4-Methyl-2-pentanone (MIBK)	108-10-1	4.0		
trans-1,3-Dichloropropene	10061-02-6	0.5		X
1,1,2-Trichloroethane	79-00-5	0.5	X	X
Toluene	108-88-3	0.5	X	X
2-Hexanone	591-78-6	4.0		
Tetrachloroethene	127-18-4	0.5	X	X
1,3-Dichloropropane	142-28-9	0.5		X

Compound Name	CAS No.	QL, ug/L	Regulated	Routinely Report
Chlorodibromomethane*	124-48-1	0.5	X	X
1,2-Dibromoethane (EDB)	106-93-4	0.5		X
Chlorobenzene	108-90-7	0.5	X	X
1,1,1,2-Tetrachloroethane	630-20-6	0.5		X
Ethylbenzene	100-41-4	0.5	X	X
m&p-Xylene	106-42-3	1.0	X	X
o-Xylene	95-47-6	0.5	X	X
Styrene	100-42-5	0.5	X	X
Bromoform*	75-25-2	0.5	X	X
Isopropylbenzene	98-82-8	0.5		X
Bromobenzene	108-86-1	0.5		X
1,1,2,2-Tetrachloroethane	79-34-5	0.5		X
1,2,3-Trichloropropane	96-18-4	0.5		X
Propylbenzene	103-65-1	0.5		X
2-Chlorotoluene	95-49-8	0.5		X
4-Chlorotoluene	106-43-4	0.5		X
1,3,5-Trimethylbenzene	108-67-8	0.5		X
tert-Butylbenzene	98-06-6	0.5		X
1,2,4-Trimethylbenzene	95-63-6	0.5		X
sec-Butylbenzene	135-98-8	0.5		X
1,3-Dichlorobenzene	541-73-1	0.5		X
1,4-Dichlorobenzene	106-46-7	0.5	X	X
p-Isopropyltoluene	99-87-6	0.5		X
1,2-Dichlorobenzene	95-50-1	0.5	X	X
Butylbenzene	104-51-8	0.5		X
1,2-Dibromo-3-chloropropane	96-12-8	2.0		X
1,2,4-Trichlorobenzene	120-82-1	0.5	X	X
Hexachlorobutadiene	87-68-3	0.5		X
Naphthalene	91-20-3	0.5		X
1,2,3-Trichlorobenzene	87-61-6	0.5		X
Surrogate Compounds				
1,2-Dichloroethane-d4				
Toluene-d8				
4-Bromofluorobenzene				
1,2-Dichlorobenzene-d4				
Internal Standards				
Dichloromethane-d2				
Fluorobenzene				
Chlorobenzene-d5				

* Trihalomethanes

APPENDIX C.
QUALITY CONTROL MEASURES AND CRITERIA

<table>
<tr><th>ANALYSIS</th><th>CRITERIA</th><th>Frequency</th></tr>
<tr><td>MS Calibration</td><td><table><tr><th>Mass</th><th>Target % of Mass 69</th></tr><tr><td>50</td><td>0.3-5</td></tr><tr><td>69</td><td>100</td></tr><tr><td>131</td><td>20-120</td></tr><tr><td>219</td><td>20-120</td></tr><tr><td>414</td><td>0.3-10</td></tr><tr><td>502</td><td>0.3-10</td></tr></table></td><td>With Every ICAL</td></tr>
<tr><td>MS Mass Axis</td><td>Calibrate the Mass Axis of the MS prior to analyzing the BFB standard. Adjust the EM voltage as necessary.</td><td>Each day that samples are analyzed</td></tr>
<tr><td>GC/MS System Performance Check (BFB analysis)</td><td>The ion abundance ratios must meet the following criteria.<table><tr><th>Mass</th><th>Relative Ion Abundance</th></tr><tr><td>50</td><td>15 - 40 % of mass 95</td></tr><tr><td>75</td><td>30 - 60 % of mass 95</td></tr><tr><td>95</td><td>Base peak, 100 % relative abundance</td></tr><tr><td>96</td><td>5 - 9 % of mass 95</td></tr><tr><td>173</td><td>< 2 % of mass 174</td></tr><tr><td>174</td><td>>50 % of mass 95 (Mass 95 must be base peak)</td></tr><tr><td>175</td><td>5 - 9 % of mass 174</td></tr><tr><td>176</td><td>> 95 but < 101 % of mass 174</td></tr><tr><td>177</td><td>5 - 9 % of mass 176</td></tr></table>All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be greater than that of m/z 95.</td><td>Once every 12-hours</td></tr>
<tr><td>Initial Calibration (1)</td><td>Reported analytes should meet the maximum %RSD of 20. Data must be flagged for analytes not within the acceptance limits. If a sample is for drinking water compliance, all regulated compounds must meet QC criteria.</td><td>As Needed</td></tr>
<tr><td>Second Source Calibration Verification (1)</td><td>Recovery for of reported analytes must be within 70-130%. Data must be flagged as failing initial calibration criteria for analytes not within the acceptance limits. If a sample is for drinking water compliance, all regulated compounds must meet QC criteria.</td><td>With Every ICAL</td></tr>
</table>

Continuing Instrument Calibration Verification (1)	The absolute value of the %D of all reported analytes should be ≤ 30%. Internal standard retention time should be within 30 seconds from that in the mid-point standard level of the most recent initial calibration. EICP area for any of the internal standards should be within (-50% to +100%) from that in the mid-point standard level of the most recent initial calibration sequence. If a sample is for drinking water compliance, all regulated compounds must meet QC criteria. Data must be flagged for analytes not within the acceptance limits.	Once every 12-hours
Low Level Calibration Verification (also QLS) (1)	The percent recovery for the reported analytes should be between 60 to 140 percent of the actual concentration. Data must be flagged for analytes not within the acceptance limits.	Once every 12-hours
Method Blank (MB)	The MB is acceptable if it contains less than one-half the quantitation limit (QL) of all target compounds. Data must be flagged for analytes not within the acceptance limits.	Once every 12-hours
Target Analytes	All ions present in the standard or reference mass spectrum at a relative intensity of 20 % of the most abundant ion should be present in the sample spectrum. The relative intensities of the ions in the sample mass spectrum should agree within 30% of the relative intensities of those ions in the standard mass spectrum. For example, an ion with an abundance of 50% in the standard spectrum can have abundance between 20% and 80% in the sample spectrum.	NA
Sample Internal Standards	Compare the IS retention times and areas in the field and QC samples analyzed within the 12-hour analytical period to the associated 12-hour CCV standard. The retention time for any internal standard should be within 0.5 minute. The total area of internal standard should be recovered within 30% from the associated 12-hour CCV standard. Data must be flagged for analytes not within the acceptance limits.	NA
Surrogates	See Table Below. Data must be flagged for analytes not within the acceptance limits.	NA

LCS [1]	Reported analytes should meet the acceptance criteria or the batch may require re-extraction. Refer to the tables below for control limits. Data must be flagged for analytes not within the acceptance limits. If a sample is for drinking water compliance, all regulated compounds must meet QC criteria.	Once every 12-hours
MS/MSD [1]	Refer to the tables below for control limits. Flag outliers. Data must be flagged for analytes not within the acceptance limits.	One per SDG

[1] Up to 10 % of the compounds may fail to meet these criteria, but if the samples are for drinking water compliance, all regulated compounds must meet all QC criteria.

Quantitation Ions, Surrogates, and Internal

Compound Name	IS Reference	Surrogate Reference	Primary Ion, m/z
Dichlorodifluoromethane	1	1	85
Chloromethane	1	1	50
Vinyl chloride	1	1	62
Bromomethane	1	1	94
Chloroethane	1	1	64
Trichlorofluoromethane	1	1	101
1,1-Dichloroethene	1	1	96
1,1,2-Trichloro-1,2,2-trifluoroethane	1	1	101
Acetone	1	1	43
Carbon disulfide	1	1	76
Dichloromethane	1	1	84
tert-Butyl alcohol	1	1	59
trans-1,2-Dichloroethene	1	1	96
tert-Butyl methyl ether (MTBE)	1	1	73
1,1-Dichloroethane	1	1	63
Diisopropyl ether	1	1	45
Ethyl *tert*-butyl ether	1	1	59
2,2-Dichloropropane	1	1	77
cis-1,2-Dichloroethene	1	1	96
2-Butanone (MEK)	1	1	43
Bromochloromethane	1	1	128
Chloroform	1	1	83
1,1,1-Trichloroethane	2	1	97
Tert-Amyl methyl ether	2	1	73
1,1-Dichloropropene	2	1	75
Benzene	2	2	78
1,2-Dichloroethane	2	1	62
Carbon tetrachloride	2	1	117
Trichloroethene	2	1	95
1,2-Dichloropropane	2	1	63
Dibromomethane	2	3	93
Bromodichloromethane	2	1	83

Compound Name	IS Reference	Surrogate Reference	Primary Ion, m/z
cis-1,3-Dichloropropene	2	1	75
4-Methyl-2-pentanone (MIBK)	3	3	43
trans-1,3-Dichloropropene	2	1	75
1,1,2-Trichloroethane	2	3	83
Toluene	3	2	92
2-Hexanone	3	3	43
Tetrachloroethene	3	3	166
1,3-Dichloropropane	3	3	76
Chlorodibromomethane	3	3	129
1,2-Dibromoethane (EDB)	3	3	107
Chlorobenzene	3	3	112
1,1,1,2-Tetrachloroethane	3	3	131
Ethylbenzene	3	2	91
m&p-Xylene	3	2	106
o-Xylene	3	2	106
Styrene	3	2	104
Bromoform	3	3	173
Isopropylbenzene	3	2	105
Bromobenzene	3	2	156
1,1,2,2-Tetrachloroethane	3	3	83
1,2,3-Trichloropropane	3	3	75
Propylbenzene	3	2	91
2-Chlorotoluene	3	3	91
4-Chlorotoluene	3	3	91
1,3,5-Trimethylbenzene	3	2	105
tert-Butylbenzene	3	2	119
1,2,4-Trimethylbenzene	3	2	105
sec-Butylbenzene	3	2	105
1,3-Dichlorobenzene	3	3	146
1,4-Dichlorobenzene	3	3	146
p-Isopropyltoluene	3	2	119
1,2-Dichlorobenzene	3	3	146
Butylbenzene	3	2	91
1,2-Dibromo-3-chloropropane	3	3	75
1,2,4-Trichlorobenzene	3	3	180
Hexachlorobutadiene	3	3	225
Naphthalene	3	2	128
1,2,3-Trichlorobenzene	3	3	180
Surrogate Compounds			
1,2-Dichloroethane-d4	2	1	65
Toluene-d8	3	2	98
4-Bromofluorobenzene	3	3	174
1,2-Dichlorobenzene-d4	3	4	152
Internal Standards			
Dichloromethane-d2	1	-	53
Fluorobenzene	2	-	96
Chlorobenzene-d5	3	-	117

LCS and MS/MSD QC Criteria (based on laboratory historical data from June 20, 2016 to September 8, 2016 at 99% confidence)[1]

Analyte	LCS Recovery, %		MS/MSD Recovery, %		MS/MSD, RPD
Dichlorodifluoromethane	63	136	23	150	50
Chloromethane	69	129	53	150	50
Vinyl chloride	70	130	58	150	50
Bromomethane	53	143	43	150	50
Chloroethane	83	117	69	142	37
Trichlorofluoromethane	75	125	62	150	49
1,1-Dichloroethene	70	130	70	143	36
1,1,2-Trichloro-1,2,2-trifluoroethane	71	138	77	150	40
Acetone	56	118	38	132	47
Carbon disulfide					
Dichloromethane	70	130	86	111	12
tert-Butyl alcohol					
trans-1,2-Dichloroethene	70	130	75	135	30
tert-Butyl methyl ether (MTBE)	67	120	75	117	21
1,1-Dichloroethane	69	126	80	124	22
Diisopropyl ether					
Ethyl tert-butyl ether					
2,2-Dichloropropane	43	144	20	150	50
cis-1,2-Dichloroethene	70	130	71	138	33
2-Butanone (MEK)	58	124	55	127	36
Bromochloromethane	72	126	80	129	25
Chloroform	70	130	72	135	31
1,1,1-Trichloroethane	70	130	58	133	38
Carbon tetrachloride	70	130	56	144	44
1,1-Dichloropropene	81	110	76	121	22
Benzene	70	130	73	121	24
1,2-Dichloroethane	70	130	81	110	13
tert-Amyl methyl ether					
Trichloroethene	70	130	84	118	17
1,2-Dichloropropane	70	130	79	117	19
Dibromomethane	77	119	82	118	18
Bromodichloromethane	70	130	84	114	15
cis-1,3-Dichloropropene	63	119	64	112	24
4-Methyl-2-pentanone (MIBK)					
Toluene	70	130	82	118	18
trans-1,3-Dichloropropene	64	119	64	110	22
1,1,2-Trichloroethane	70	130	82	121	20
Tetrachloroethene	70	130	53	150	50
1,3-Dichloropropane	78	121	83	118	18
2-Hexanone					
Chlorodibromomethane	70	130	76	126	25
1,2-Dibromoethane (EDB)	80	116	84	115	15
Chlorobenzene	70	130	85	114	15
1,1,1,2-Tetrachloroethane	77	113	82	111	15

1. Regulated compounds, shown in bold, have LCS acceptance limits of 70-130% recovery per Method 524.2.

Analyte	LCS Recovery, %		MS/MSD Recovery, %		MS/MSD, RPD
Ethylbenzene	70	130	80	120	20
m&p-Xylene	70	130	75	124	24
o-Xylene	70	130	82	114	16
Styrene	70	130	78	116	19
Bromoform	70	130	64	131	34
Isopropylbenzene	85	112	77	125	24
Bromobenzene	85	110	87	110	11
1,1,2,2-Tetrachloroethane	70	129	73	132	29
1,2,3-Trichloropropane	69	124	74	125	25
Propylbenzene	86	114	76	127	26
2-Chlorotoluene	81	113	78	117	19
4-Chlorotoluene	81	113	76	117	21
1,3,5-Trimethylbenzene	82	115	74	123	25
tert-Butylbenzene	85	113	70	127	28
1,2,4-Trimethylbenzene	79	117	76	121	22
sec-Butylbenzene	80	124	67	139	36
1,3-Dichlorobenzene	80	111	79	114	18
p-Isopropyltoluene	80	121	65	136	35
1,4-Dichlorobenzene	70	130	73	120	24
1,2-Dichlorobenzene	70	130	81	112	16
Butylbenzene	78	124	61	141	40
1,2-Dibromo-3-chloropropane	64	120	56	132	38
1,2,4-Trichlorobenzene	70	130	68	117	25
Hexachlorobutadiene	65	123	65	124	29
Naphthalene	67	113	60	131	35
1,2,3-Trichlorobenzene	69	114	67	120	27

Surrogate QC Criteria

Compound Name	Recovery, %	
1,2-Dichloroethane-d4	77	117
Toluene-d8	85	110
4-Bromofluorobenzene	85	110
1,2-Dichlorobenzene-d4	81	125

APPENDIX D.
RECOMMENDED INSTRUMENT PARAMETERS

PURGE & TRAP CONCENTRATOR/AUTOSAMPLER PARAMETERS

Purge and Trap Concentrator operating parameters

The operating parameters for the purge & trap concentrators. These parameters may vary slightly to optimize instrument responses except Purge Time, Purge Flow, and Desorb Time cannot be altered from the method required settings.

PARAMETER	SETTING
	Concentrator
Standby temperature	38°C
Preheat temperature	N/A
Prepurge time	N/A
Sample temperature	Ambient (off)
Purge Time*	11 minutes
Dry purge	1 minute
Purge Flow*	40 mL/min
Desorb preheat temperature	245°C
Desorb Time*	4.00 minutes @ 250°C
Bake	11 minutes @ 260°C
Auto drain	On (controlled by Autosampler)
Bake gas bypass	Off
Valve temperature	150°C
Mount temperature	40°C
Line temperature	150°C

*Do not optimize these settings.

Autosampler

The Autosampler delivers an aliquot of the water sample directly from the 40 mL sample vial into the sparge vessel on the concentrator. The Autosampler is programmed to add the internal standard and surrogate into the sample during the transfer process.

Standard loading:

1. Prepare standards and blank spikes in a 50-mL volumetric flask with acidified method blank water.
2. Gently invert three times.
3. Gently pour the standard solution into the 40-mL vial (pre-label with information about the standard), down the side of the vial, without any agitation. Overfill the vial to form an inverted meniscus. Cap the vial. Invert the vial to ensure that there are no

air bubbles present.

4. Gently place the vial in the appropriate autosampler position.
5. The autosampler will analyze a 25 mL aliquot and add 1 µL of the 125 ng/µL VOA IS/SS solution. The amount used results in the analytical equivalent of 5 µg/L.

HP/Agilent 6890 GC & HP/Agilent 5973MSD

The operating parameters for this system are listed below. Actual operating conditions may vary slightly to optimize instrument

BFB analysis

PARAMETER	SETTING
Injector temperature	200°C
Column Stability time	0.5 minutes
MS Quad	150°C
MS Source	230°C
Initial Oven Temp	110°C
Initial Oven Time	0.5 minutes
Temperature Ramp	25°C/minute for 3.6 minutes
Final Oven Temp	190°C
Final Hold Time	1.9 minutes
Inlet mode:	Split
Split vent flow:	20 mL/min
Column Flow rate	0.8 mL/min at constant flow mode
Electron Energy	70 volts (nominal)
MS Scan range	35-260 amu

VOA analysis

PARAMETER	SETTING
Injector temperature	200°C
Column Stability time	0.5 minutes
MS Quad	150°C
MS Source	230°C
Initial Oven Temp	35°C
Initial Oven Time	3.0 minutes
Temperature Ramp	8°C/minute to 120°C for 2 minutes; 25°C/minute to 195°C for 2.2 minutes
Final Oven Temp	200°C
Final Hold Time	2.0/* 5.0 minutes
Inlet mode:	Split
Split vent flow:	20 mL/min.
Column Flow rate	0.8 mL/min at constant flow mode.
Electron Energy	70 volts (nominal)
MS Scan Range	35-260 amu

Analytical system preparation:

Leak Checking

From the ChemStation Instrument Control panel of the HP 5973 MSD select View, Tune and Vacuum control.

Select Spectrum scan. Check the nitrogen (m/z 28), water (m/z 18), to FC43 (m/z 69) ratio. Ratios for ions 28 and 18 should not exceed 20% of ion 69. Values higher than indicated above are indicative of large leaks and must be corrected.

Auto Tuning

Perform an autotune of the analytical system prior to an initial calibration, whenever the mass spectrometer is shut down, or the source is cleaned.

Perfluorotributylamine (FC43) is the compound used to perform the mass calibration of the instrument. Proper tuning of the instrument is necessary to produce standardized fragmentation patterns of target and non-target compounds.

The autotune software will adjust the mass ratio, abundance, peak shape, width, isotope peak resolution, and mass assignment.

An autotune report will be generated and the parameters will be saved in ATUNE.U.

The Agilent ChemStation software requires that the FC43 spectrum meet the Criteria listed in Appendix C.

Preparation for an Initial Calibration

Perform an autotune of the analytical system prior to an initial calibration.

1. The system should be reset to default parameters as follow:
   a. From the ChemStation Instrument Control panel of the HP 5973 MSD select View, Tune and Vacuum control. Select File, Reset to Default, Autotune.
   b. If the DC polarity for the system is normally set to negative for the system, resetting the tune parameter will set it to positive. Set the parameter to negative by selecting Parameters, Manual tune, DC polarity and slide the polarity selector to negative.
2. Save the default parameters by selecting save tune, Autotune.u.
3. Autotune the system by selecting Tune, Autotune.
4. The system will generate an Autotune report.
5. Save the resulting tune file by selecting File, Save tune Value
6. The tune file name is selected as outlined in Appendix E.
7. Generate the tuning report by selecting File, Generate report.

Preparation for a Continuing Calibration

1. Perform a mass axis calibration of the analytical system prior to continuing calibration. By selecting calibrate, Mass axis.
2. Save the resulting tune file by selecting File, Save tune Value.
3. The tune file name is selected as outlined in Appendix E.
4. Generate the tuning report by selecting File, Generate report.

Manual tuning

If the system fails to meet the tuning criteria, the source may need to be cleaned or manual tuning may be required. BFB or DFTPP tuning routines may be used to correct ions ratios.

To manually tune the system, select Manual Tune from View menu in Instrument Control

view and manually tune the MSD, using ATUNE.U as reference. Adjust the parameters of Ion Focus, Entrance Lens, Repeller, Entrance Lens Offset, EM voltage etc to suit your analysis needs.

Incorporate the new tune parameters and generate today's method

1. Load a copy of the last initial calibration from C:\HPCHEM\1\Methods\Initial.
2. From the ChemStation Instrument Control panel of the HP 5973 MSD click on Select MS Tune File icon, click on the name of tune file generated today.
3. Select MS/SIM San Parameters. If necessary, adjust the EM voltage by adding or subtracting voltage relative "REL" to today's tune voltage.
4. Save the resulting method file as outlined in the as outlined in Appendix E by selecting File, Save method.

Mass Calibration:

Perform mass calibration of the analytical system prior to an initial calibration, whenever the mass spectrometer is shut down, or whenever there is a mass miss-assignment is noted. Mass calibration is performed to ensure the accurate assignment of masses to ions generated in the ion volume of the mass spectrometer.

Initial Calibration:

Prior to analyzing an initial calibration, ensure that proper system maintenance and GC/MS tuning (BFB and/or manual tune) has been performed. When the instrument is ready for analysis, perform the following steps:

1. In the ChemStation data analysis module, load the current initial calibration method from D:\MSDCHEM\Year\Methods\
2. Perform an initial calibration using the recommended concentrations listed in Section 8.2.1.
3. Update the response factors in the method using the newly acquired calibration files.
4. Update the retention time in the method using the newly acquired continuing calibration level.
5. Update the qualifier ion relative responses from the CCV calibration level.
6. Save the method as outlined in Appendix E.
7. Generate "Response Factor Report."
8. Check the calibration files listed on the "Response Factor Report" to insure that the correct files are being used.
9. Check the time and date to ensure that the correct update is used.
10. Process the SCV with the newly created initial calibration, check to make sure the "QLast Update" time and date match the "Response Factor Report"
11. Open and immediately close Chemstation Custom Reports. (Note: no Chemstation custom reports are actually used, opening and closing custom reports populates "detail.xls" which is later mined for data.)
12. Open the latest copy of C:\msdchem\custrpt\ "Full_Custom_Report.xls" Make sure automatic updates of links is enabled under options.
13. Go to the "SCV Recovery", "ICAL Area", "ICAL conc", tabs and print reports. Make sure the SCV passes acceptance criteria (Appendix C) and the ICAL areas match what is on the

Chemstation quant reports.

14. Verify that the method was updated correctly. Print the Compound List Report from ChemStation. Verify that the average response factor is used. Scrupulously check the elution order and retention times, compare them to an old ICAL if needed.
15. Copy the method to I:\RoomNumber\Instrument\Year\Methods\
16. Manually calculate a result for one surrogate in the SCV to insure that the correct RFs are being used and write the results on the quantitation report.
17. Save a hard copy of the initial calibration files so they may be copied and included in associated packages.

The analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are not contaminated. This is accomplished through the analysis of a method blank or an instrument blank.

Refer to Section 9.2.2 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

Continuing Calibration

Analyze a calibration verification standard at the beginning of each 12-hour analytical period by performing the following steps:

1. In the ChemStation data analysis module, load today's method from D:\MSDCHEM\Year\Methods.
2. Acquire the continuing calibration using today's method.
3. Quantitate the continuing calibration file.
4. Generate "Evaluate Continuing Calibration Report".
5. Compare the IS retention times and areas in the CCV standard to the mid-point standard of the most recent initial calibration. Adjust the electron multiplier (EM) voltage if needed (an increase of 50 volts will typically double the response). If the EM voltage is changed, reanalyze BFB and the CCV.
6. Manually calculate the result for one surrogate to insure that the correct RFs are being used. Record the result on the quantitation report.
7. As each run is quantitated during the day, make sure that the same date and time stamp, (e.g. "QLast Update : Mon Jul 25 08:15:58 2011"), is recorded on each file header.
8. If QLast Update time stamp changes, state the reason, repeat steps 4-7, and include the reports generated in the package.
9. Save a copy of the method to the LAN, when the data are backed up to the LAN the following day.

Refer to Section 9.2.3 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

APPENDIX E.
CHEMSTATION FILE NAMING CONVENTIONS

Files for data, methods, tunes, and sequences on ChemStation computers and the LAN are named using the following naming conventions:

Directories

On the Workstation (When available, use D: drive):

Data:	C:\MSDCHEM \1\DATA\YEAR\DATA\MMDDYYSS or
	D:\MSDCHEM\YEAR\DATA\MMDDYYSS
Methods:	C:\MSDCHEM\1\DATA\YEAR\METHODS or
	D:\MSDCHEM\YEAR\METHODS
Sequences:	C:\MSDCHEM\1\DATA\YEAR\SEQUENCE or
	D:\MSDCHEM\YEAR\SEQUENCE
Tunes:	C:\MSDCHEM\1\5973N or C:\MSDCHEM\1\5975

On the LAN:

Data:	I:\DATA\ROOM NUMBER\INSTRUMENT\YEAR\DATA\MMDDYYSS
Methods:	I:\DATA\ROOM NUMBER\INSTRUMENT\YEAR\METHODS
Sequences:	I:\ DATA\ROOM NUMBER\INSTRUMENT\YEAR\SEQUENCE
Tunes:	I:\ DATA\ROOM NUMBER\INSTRUMENT\YEAR\TUNE

Methods
MMDDYYATC

Sequence
MMDDYYCSS

Data Files
MMDDYYCSS

Tune Files
MMDDYYA

Variables

A: Enter analysis, as follow:

504	EDB
TO15	TO15
BNA	BNA
BNA (SIM)	PAH or PCP
PEST	PEST
PCB	PCB
RSK175	RSK
TPH-G	GRO
TPH-D	DRO
VOA	VOA
BFB	BFB

DFTPP DFT

C: Channel (use when applicable):
Front A
Back B
Both AB

DD: Day i.e. 01, 02, 03, ….

MM: Month i.e. 01, 02, 03, ….

SS: Sequential number 01, 02, 03, ….

T: Matrix Type (if applicable)
Water W
Solid S
Air A
Oil O
Other X

YY: Year i.e. 12 for 2012

APPENDIX F.
PREVENTATIVE MAINTENANCE REQUIREMENTS

GC Maintenance

Item	Frequency	Actions/Comments
Split vent trap	As Needed	Replace.
Inlet liner	With each ICAL	Check often. Replace when dirt is visible in the liner or if chromatography is degraded.
Liner O-rings	With each ICAL	Check often. Replace with liner or with signs of wear.
Inlet septum	With each ICAL	Check often. Replace when signs of deterioration are visible (gaping holes, fragments in inlet liner, poor chromatography, low column pressure, etc.).
Inlet Hardware	Annually	Check for leaks and clean. Check parts and replace when parts are worn, scratched, or broken.
Column Maintenance	As Needed	Remove 1/2-1 meter from the front of the column when experiencing chromatographic problems (peak tailing, decreased sensitivity, retention time changes, etc.).
Column Replacement	As needed	When trimming no longer returns chromatographic performance.
Ferrules		Replace ferrules when changing columns and inlet/detector parts.
Archon/Purge System Lines	As needed	Bake out transfer and purge system line. Clean with organic free water if necessary.
Trap	As needed	Replace with loss of performance.
EM voltage	As needed	If an overall change in sensitivity (area counts in CCV in comparison to most recent ICAL), the EM voltage may need adjusting.

MS Maintenance

Task	Every Week	Every 6 Months	Every Year	As Needed
Tune the MSD				✓
Check the foreline pump oil level	✓			
Check FC43 level		✓		
Replace the foreline pump oil		✓		
Clean the ion source				✓
Check the carrier gas traps on the GC				✓
Replace worn out parts				✓
Lubricate sideplate or vent valve O-rings				✓

APPENDIX G.
METHOD PERFORMANCE

Volatile Organic Compound Analysis in Water
June 20, 2016 to September 8, 2016

Analyte	Number of Measurements	Mean Recovery, %	Standard Deviation (σ)	95% Confidence Interval (2 σ)	
Dichlorodifluoromethane	37	99.3	12.1	63	136
Chloromethane	37	99.0	9.9	69	129
Vinyl chloride	37	99.1	6.1	81	117
Ethylbenzene	37	97.4	3.2	88	107
Bromomethane	37	97.9	15.0	53	143
Chloroethane	37	99.9	5.6	83	117
Trichlorofluoromethane	37	100.2	8.3	75	125
1,1-Dichloroethene	37	97.5	7.0	77	118
1,1,2-Trichloro-1,2,2-trifluoroethane	37	104.6	11.2	71	138
Acetone	37	87.1	10.3	56	118
Carbon disulfide					
Dichloromethane	37	95.1	5.1	80	110
tert-Butyl alcohol					
trans-1,2-Dichloroethene	37	98.3	7.3	76	120
tert-Butyl methyl ether (MTBE)	37	93.1	8.8	67	120
1,1-Dichloroethane	37	97.2	9.4	69	126
Diisopropyl ether					
Ethyl tert-butyl ether					
2,2-Dichloropropane	36	93.3	16.9	43	144
cis-1,2-Dichloroethene	36	98.9	8.2	74	124
2-Butanone (MEK)	37	90.6	11.0	58	124
Bromochloromethane	37	99.2	8.9	72	126
Chloroform	37	98.6	7.6	76	121
1,1,1-Trichloroethane	37	93.3	6.4	74	113
Carbon tetrachloride	37	94.8	7.4	73	117
1,1-Dichloropropene	37	94.4	4.4	81	108
Benzene	37	96.4	3.9	85	108
1,2-Dichloroethane	37	94.3	6.1	76	113
tert-Amyl methyl ether					200
Trichloroethene	37	96.1	3.3	86	106
1,2-Dichloropropane	37	97.0	5.5	81	113
Dibromomethane	37	97.8	6.9	77	119
cis-1,3-Dichloropropene	37	90.9	9.3	63	119
Bromodichloromethane	37	97.2	6.1	79	115
4-Methyl-2-pentanone (MIBK)					
Toluene	37	97.5	3.5	87	108
Tetrachloroethene	37	95.2	4.4	82	109
trans-1,3-Dichloropropene	37	91.7	9.2	64	119
1,1,2-Trichloroethane	37	100.4	7.2	79	122
1,2-Dibromoethane (EDB)	37	97.8	6.0	80	116

Analyte	Number of Measurements	Mean Recovery, %	Standard Deviation (σ)	95% Confidence Interval (2 σ)	
1,3-Dichloropropane	37	99.1	7.2	78	121
2-Hexanone					
Chlorodibromomethane	37	99.6	9.2	72	127
Chlorobenzene	37	97.2	3.2	88	107
1,1,1,2-Tetrachloroethane	37	95.2	5.9	77	113
m&p-Xylene	37	97.4	4.9	83	112
o-Xylene	37	96.1	3.8	85	108
Styrene	37	98.2	4.9	84	113
Bromoform	37	98.7	11.2	65	132
Isopropylbenzene	37	98.4	4.4	85	112
Bromobenzene	37	96.0	3.7	85	107
1,1,2,2-Tetrachloroethane	37	99.8	9.8	70	129
1,2,3-Trichloropropane	37	96.7	9.2	69	124
Propylbenzene	37	99.8	4.7	86	114
2-Chlorotoluene	37	97.1	5.3	81	113
4-Chlorotoluene	37	96.6	5.3	81	113
1,3,5-Trimethylbenzene	37	98.2	5.5	82	115
tert-Butylbenzene	37	98.8	4.7	85	113
1,2,4-Trimethylbenzene	37	98.0	6.3	79	117
sec-Butylbenzene	37	102.1	7.4	80	124
1,3-Dichlorobenzene	37	95.5	5.1	80	111
1,4-Dichlorobenzene	37	95.0	5.8	78	112
p-Isopropyltoluene	37	100.5	6.9	80	121
1,2-Dichlorobenzene	37	94.9	6.0	77	113
Butylbenzene	37	101.1	7.8	78	124
1,2-Dibromo-3-chloropropane	37	91.9	9.3	64	120
1,2,4-Trichlorobenzene	37	91.1	6.6	71	111
Hexachlorobutadiene	37	94.1	9.7	65	123
Naphthalene	37	89.8	7.6	67	113
1,2,3-Trichlorobenzene	37	91.4	7.5	69	114

APPENDIX H.
REVISION HISTORY

STANDARD OPERATING PROCEDURE: 354
Revision: 12, Effective: 10/17/2016

Volatile Organic Compound Analysis in Water

Revision	Effective Date	Description
8	04/21/08	1. Added Method 8260B as a reference method. 2. Added requirement that all equipment, standards, reagents, and supplies must meet technical & QC requirements of the reference method. 3. Added requirement to prepare standards and instrument and batch QC samples in acidified organic-free water. 4. Changed LCS %R QC Limits to 70 – 130% for regulated compounds. 5. Added option to purge BFB. 6. Changed RRT criteria for analyte identification from relative to absolute. 7. Deleted requirement to re-analyze samples containing < 5 times MB amount for common laboratory contaminants. 8. Revised Sections 8.2.1 and 8.2.2 and Appendix D to clarify and reflect current practice.
9	11/27/09	1. Revised Appendix D to require adherence to instrument operating conditions specified in the reference method. 2. Minor changes throughout to update SOP to current requirements of SOP 850 for format.
10	03/01/13	1. Revised Appendix C to require adherence to drinking water criteria. 2. Moved ChemStation specific instructions to Appendix D to improve readability. 3. Minor changes throughout to update SOP to current requirements of SOP 850 for format.
11	02/03/14	Limited revision to address the following: 1. Added EST purge and trap and EST trap to equipment list. 2. Added previously omitted 10% allowance for CCV outliers to Appendix C. 3. Added purge and trap parameters to Appendix D and EST operating parameters to Appendix D. 4. General edits throughout to comply with current SOP format.
12	10/17/16	Limited revision to address the following: 1. Removed preparation of standards in 50-mL syringe in Section 8.2.1, Section 8.3.2, and Appendix D. 2. Added instructions regarding peroxide-forming chemicals

	and reference to SOP 785. 3. Removed run log example and references to it. 4. Updated method performance and QC limits. 5. Minor changes throughout.